An *In situ* Surface X-Ray Diffraction Study on the Electrochemical Deposition of Ni on Au(111)

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Introduction

The technological relevance of Ni electrodes and Ni plating has increased significantly in recent years with the growing interest in fuel cells and rechargeable batteries. Most of the science relevant to the processes involved in these technologies occurs at the metal-electrolyte interface. Therefore techniques that can probe this interface (STM, AFM, SXS) have seen rapid development over the last decade.

The results presented here represent the continuation of a project looking at bulk Ni crystals, Ni oxides, Ni hydrides and the deposition of Ni films onto single metal crystals. This paper deals with the electrodeposition of Ni from electrolyte onto a Au(111) single crystal surface.

Experimental procedure

The SXRD measurements were carried out on the XMaS CRG at the ESRF Grenoble, and beamlines 16.3 and 9.4 at the SRS Daresbury. The Au(111) single crystal was prepared initially by mechanically polishing with decreasing grades of diamond paste and finished with a 0.05µm alumina. The crystal was then electropolished and flame annealed for several cycles to produce a well ordered (111) surface. After preparation the crystal was mounted in a specially designed electrochemical cell which fits into a standard Huber goniometer head. The cell was filled with N_2 purged modified Ni Watts bath electrolyte (containing H_3BO_3, HCl, and $NiSO_4$) and covered with a polypropylene film. A cyclic voltammogram was taken to characterize the system and establish the deposition potential for Ni. The polypropylene film was then deflated trapping a thin layer of electrolyte over the crystal surface, and SXRD measurements were made both before and after Ni deposition. A more detailed experimental method can be found in reference 1.

Results and discussion

Reciprocal space scans along high symmetry directions performed before Ni deposition (fig.1 triangular data points) showed a 'clean' Au(111) surface with no apparent reconstruction. The peak at the center of the scan is due to the (1 0 L) CTR and no other diffraction features could be seen in close proximity to this peak. In the scans performed after Ni deposition however, (fig.1 circular data points) the intensity at (1 0 0.2) decreases, and a second peak appears at approximately (1.02 0.02 0.2). The Au(111) surface is known to reconstruct into a 'herring bone' structure with three rotational domains of a (23 x √3) unit cell [2]. The position of the new peak is consistent with the scattering expected from the reconstructed Au(111) surface. The inset plot, however, shows the time dependent growth of the reconstruction peak, with intensity still increasing after 1200 seconds. In comparison, previous studies of the Au(111) reconstruction [2] showed that the reconstruction formed in approximately 20-120 seconds. The order of magnitude difference suggests a growth process, due to Ni deposition. In addition a scan of the incident x-ray energy in the region of 8.36 keV, (the K absorption edge for Ni), gave changes in the scattered intensity that were consistent with Ni being incorporated into the Au reconstruction. A mixed reconstruction has been suggested by a previous STM study [3], with Ni depositing substitutionally at the faulted 'elbow' sites of the herring bone. Ni deposition then continues across the surface as needle growth seeded from the substitutional positions. The STM measurements however can provide no further information about the interface structure after a full monolayer of Ni is deposited. In contrast contour plots and CTR measurements showed that the reconstruction was maintained even after bulk Ni deposition. Au CTRs were also measured at energies close to the Ni K-edge and modeling has shown that Ni atoms had been taken into the reconstructed phase. After bulk deposition, diffraction was observed for a Ni(111)-type structure aligned with the Au(111) substrate. Thus the reconstructed phase provides the interface between the Au lattice and the relaxed Ni(111) film.

References

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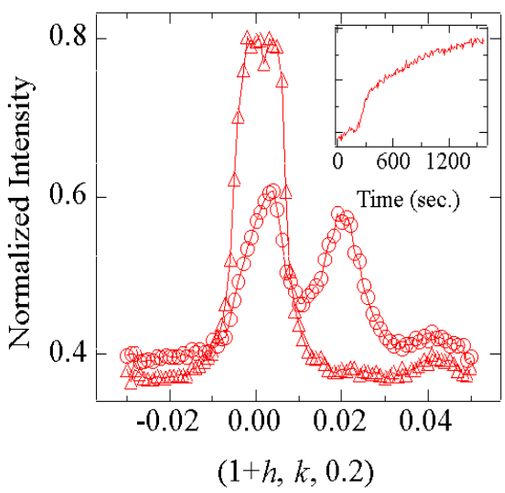

Fig. 1.
Reciprocal space scans in the <110> direction for Au(111) near the (10L) CTR. Triangular and circular data points measured before and after Ni deposition respectively.
The insert shows time-dependence of the intensity at (1.02 0.02 0.2).